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Techniques used in EPA Method 8, the source test method for acid mist and sulfur dioxide emissions from sulfuric acid plants, have been evaluated. Evidence is shown that trace amounts of peroxides in isopropyl alcohol result in the conversion of sulfur dioxide to sulfate and cause positive errors in acid mist values. Methods for measuring and purifying IPA are described. No conversion of sulfur dioxide to sulfate on filters or filter supports were observed. Collection efficiencies of train components are described and two alternate indicators are evaluated. Solid ammonium sulfates's use as audit samples is discussed.

Field testing is also described in which paired-probe techniques were employed. They showed that, when sulfur trioxide is absent from the effluent streams, acid mist is efficiently collected by a single filter, even when the isopropyl alochol-containing impinger is eliminated. Both ammonia and dimethyl analine, which are employed as gas scrubbers, cause sulfur dioxide to be retained in the isopropyl alcohol and result in large positive interferences in acid mist values. Ferric oxide, present in the effluents of steel pickling operations, causes a large negative interference in acid mist values.

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AN EVALUATION STUDY OF EPA METHOD 8

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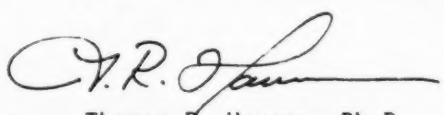
FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

This investigation was conducted at the request of the Office of Air Quality Planning and Standards. A test method for the measurement of acid mist and sulfur dioxide emissions from sulfuric acid plants was evaluated. The work was carried out to answer certain questions that arose in earlier studies in which high acid mist values occurred together with low sulfur dioxide measurements. Those studies suggested that some conditions may have existed that caused the oxidation of sulfur dioxide to sulfate in the sample collection apparatus. The present investigation included a study of operating characteristics and the efficiency of components in the sampling system as well as of some of the analytical processes. Both laboratory and field investigations were conducted.



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ABSTRACT

Techniques used in EPA Method 8, the source test method for acid mist and sulfur dioxide emissions from sulfuric acid plants, have been evaluated. Evidence was found that the presence of trace amounts of peroxides in isopropyl alcohol results in the conversion of sulfur dioxide to sulfate and causes a significant positive error in acid mist values. Such peroxide contamination was found to be common. Methods are described for measuring peroxide spectrophotometrically and for removing them over a column of activated alumina. No conversion of sulfur dioxide to sulfate was observed in peroxide-free isopropyl alcohol, in sintered glass filter supports or on glass fiber filters. Efficient collection of sulfur dioxide took place in the hydrogen peroxide-containing impingers specified in Method 8. Sulfuric acid mist and sulfur trioxide were efficiently collected by a single impinger containing isopropyl alcohol in combination with a filter. Two alternate indicators, sulfanazo III and xylene cyanol FF, were studied and found to be inferior to thorin. Solid ammonium sulfate was shown to be useful for the preparation of audit samples.

In field testing, paired-probe techniques showed that, when sulfur trioxide is absent, acid mist is efficiently collected by a single filter even when the isopropyl alcohol-containing impinger is eliminated. Both ammonia and diemthylanaline, which are employed as gas scrubbers, cause sulfur dioxde to be retained in isopropyl alcohol and result in large positive interferences in acid mist values. Ferric oxide, present in the effluents of steel pickling operations, causes a large negative interference in acid mist values.

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SECTION 1

INTRODUCTION

In its efforts to limit the discharge of harmful sulfur compounds into the environment, the U.S. Environmental Protection Agency has promulgated standards of performance for new stationary sources which include sulfuric acid plants and which limit the discharge of sulfuric acid mist and sulfur dioxide into the atmosphere (1). An appendix to that regulation (see Appendix A) specifies a test procedure to determine compliance with the standard. This test, Reference Method 8, is the subject of the present study. It was conducted in the Quality Assurance Division of the Environmental Monitoring Systems Laboratory, which is responsible for evaluating and standardizing EPA test methods. Since promulgation of Reference Method 8, the need for a number of changes has become apparent. As a result, several changes to further clarify the method and improve its reliability and accuracy have been incorporated (2).

The test procedure under consideration is designed to separate and measure sulfuric acid mist (including sulfur trioxide) (SO_3) and sulfur dioxide (SO_2). A measured volume of gas sample is isokinetically extracted from the stack and passed through an impinger-filter train, where sulfuric acid (H_2SO_4) mist is collected in isopropanol (IPA) solution and onto a glass fiber filter, while sulfur dioxide is oxidized to sulfate in hydrogen peroxide (H_2O_2) solution. Both fractions are then analyzed by the barium-thorin method (3). This method was reported to have a detection limit of 0.05 mg/m^3 for sulfur trioxide and 1.2 mg/m^3 for sulfur dioxide (4). However, the present study is primarily concerned with the adequacy of the method in the concentration ranges determined by the performance standard. The latter (1) is stated in terms of allowable quantities of acid mist and SO_2 that may be emitted per ton of acid produced (2 Kg SO_2/metric ton and 0.075 Kg of acid mist/metric ton). When these standards are related to the proportion of dilution air commonly employed in the

manufacturing process (5,6), they correspond to gaseous concentrations of acid mist and SO_2 in the 15 to 30 mg/m^3 and 400 to 800 mg/m^3 ranges, respectively. (See Appendix B for details.)

The present investigation was carried out to answer certain questions that arose during a recent collaborative test (4). In that study, there were a number of observations where high acid mist values occurred together with low SO_2 measurements, at a frequency greater than due to chance alone. It was felt that some conditions might have existed to cause the simultaneous occurrence o these values; for example, during SO_2 oxation to sulfate in the sample collection apparatus. Some information about the operating characteristics and collection efficiencies of various train components under simulated field conditions was also expected to result from this investigation.

SECTION 2

CONCLUSIONS

Evidence was found revealing that the presence of trace amounts of peroxides in isopropyl alcohol (IPA) results in the conversion of sulfur dioxide to sulfate. The observed conversion, although too small to effect sulfur dioxide measurement, produced sufficient H_2SO_4 to cause a significant positive error in the acid mist values. Such contamination was common in reagent grade IPA. The presence of peroxides was determined by shaking with 10 percent potassium iodide (KI) solution and reading the absorbance at 352 nm. Peroxide contamination was removed from IPA by passing it through a column of activated alumina.

No conversion of SO_2 to sulfate was observed in peroxide-free IPA, in the sintered glass filter support disc, or on the glass fiber filter. Investigation of the latter component included the use of heated gas streams and the selection of filter paper from several different suppliers. Furthermore, the presence of acid on the filter paper did not catalyze the conversion of SO_2 to sulfate.

Efficient collection of SO_2 took place in the H_2O_2-containing impingers specified in Method 8.

Sulfuric acid mist and SO_3 were efficiently collected by a single IPA impinger in combination with a filter. No variation was observed over a range of flow rates, temperatures, and concentrations or with the various filter papers employed. However, for efficient SO_3 collection, the IPA level must be maintained above the impinger impaction plate, since SO_3 must be hydrated to acid mist to allow its collection on the glass fiber filter.

Two alternate indicators were studied and found unsuitable. These were sulfanazo III and mixtures of thorin and xylene cyanol FF. Both were strongly absorbed on the barium sulfate ($BaSO_4$) precipitate, producing color changes that obscured the end point.

In field testing, paired probe techniques were employed to compare a standard Method 8 train with several train variations. These studies showed that, when SO_3 is absent from the gas stream, acid mist is efficiently collected by a single filter even when the IPA-containing impinger is eliminated. Ammonia (NH_3) and dimethyl analine (DMA) vapors collected in the IPA-containing impinger cause SO_2 retention and result in large positive interferences in acid mist values. Both NH_3 and DMA are used in sulfuric acid plant tail gas scrubbers. Ferric oxide (Fe_2O_3), which is present in the effluents of steel pickling operations, causes a large negative interference in acid mist values.

Solid ammonium sulfate ($[NH_4]_2SO_4$) has proven to be a useful material in the preparation of audit samples for use in Method 8 analysis.

SECTION 3

EXPERIMENTAL PROCEDURES

LABORATORY PROCEDURES

Gaseous mixtures of SO_2 in dry air or nitrogen (N_2) were prepared using a model SP-492 Matheson Dyna-blender. The SO_2 employed was Linde, anhydrous grade. Compressed air was purified by passage through a glass wool filter, a silica gel impinger and a CRS Drierite/Molecular Sieve filter. In some instances when the generated atmosphere was required to have a moisture content, the silica gel impinger and CRS filter were replaced with an impinger containing distilled water. Liquid air nitrogen was used without additional treatment. The Dyna-blender was capable of preparing three component mixtures in the 20 to 50,000 ppm range at flow rates of 200 l/min. Its calibration was checked over a 4 to 200 l/min range using a model P-1900 chain compensated Collins Spirometer. Deviations of less than 1 percent were encountered. Atmospheres containing SO_3 were generated using the schematically shown system in Figure 1. Dry nitrogen was passed through a Hastings model ALF2KX Mass Flowmeter and into an impinger containing 30 percent oleum. The resulting SO_3-containing gas was mixed with the output of the Dyna-blender and then passed through a series of mixing chambers. A glass fiber filter removed any acid mist from the gas stream. Acid mist was generated using the same system, except that moisture was added to hydrate the SO_3 and the mist-knockout filter was removed. One series of experiments examined the collection of acid mist both before and after the addition of SO_2. This study utilized the manifold shown in Figure 2 from which parallel samples were extracted, one upstream and one downstream, from the point of SO_2 addition. Appropriate correction factors were applied to account for the dilution caused by the SO_2.

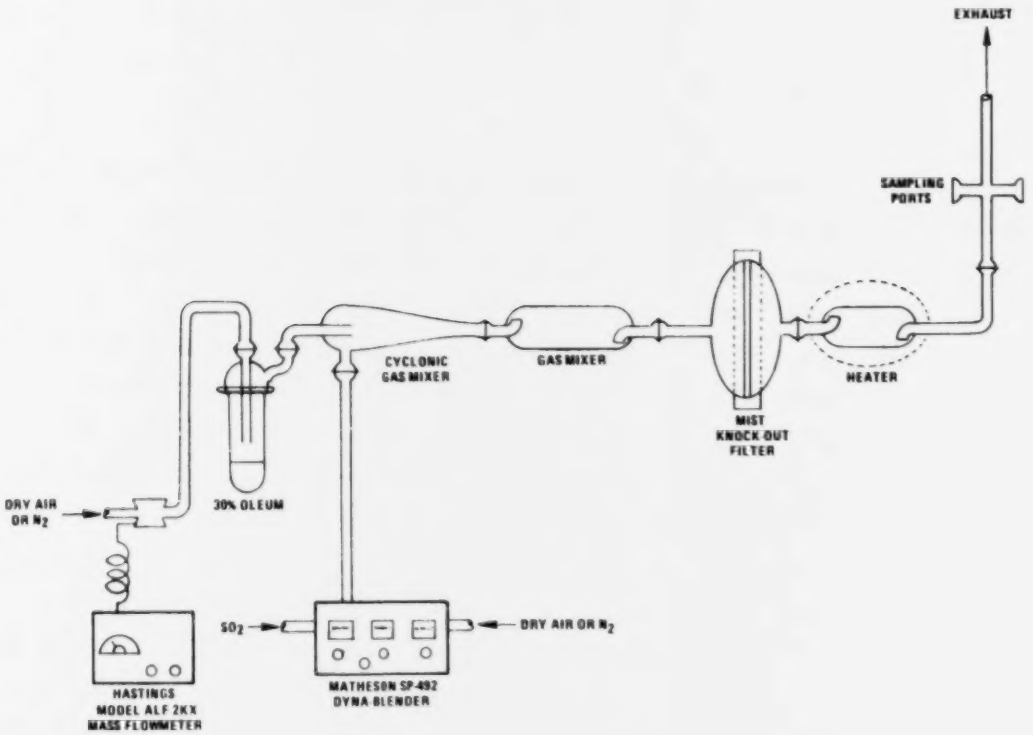

Figure 1. Acid mist and sulfur trioxide effluent simulator.

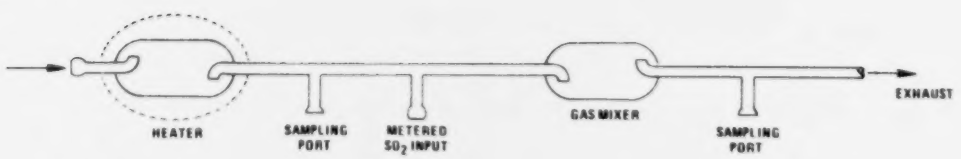

Figure 2. Sulfur dioxide test sampling port arrangement.

The analytical and sampling procedures specified in Method 8 (described in Appendix A) were followed throughout this study. Only those modifications noted below were employed. The essential features of Method 8 rely on the following sequence.

- A measured volume of gas is passed through a Greenburg-Smith impinger containing 80 percent isopropanol-water solution and then through a glass fiber filter.

- Sulfuric acid mist is collected in these components; any SO_3 present is hydrated to H_2SO_4 and also collected.

- The combined filter extract and impinger solution are analyzed for sulfate by the barium-thorin method.

- The gas then passes through two additional Greenburg-Smith impingers containing 3 percent H_2O_2 solution. This solution absorbs SO_2 gas and oxidizes it to H_2SO_4.

- These solutions are combined and are also subjected to barium-thorin analysis.

One variation practiced throughout this study consisted in the separate determination of the sulfate content of the individual train components. In some instances, the sulfate collecting impinger-filter combination was supported by an additional combination in order to determine if SO_3 had escaped collection.

J. T. Baker analyzed grade thorin and desicchlora (anhydrous $Ba[ClO_4]_2$) were employed in the analysis. The titrant was standardized using Fisher Certified standard H_2SO_4 solution. The isopropyl alcohol employed came from several sources.

The pH of glass fiber filter paper was determined by placing a 9 sq in. sample of the paper in a 125 ml glass stoppered Erlenmeyer flask together with

a 1 in by 3/8 in teflon sheathed stirrer bar and 15 ml of 0.05 M potassium chloride (KCl) solution made from carbon dioxide (CO_2) free, deionized water. The mixture was held at 22 $\pm$ 1°C and stirred for 10 min at 60 rpm, after which the pH was measured using a Beckman Expandomatic TM pH meter using a model 41263 glass electrode.

FIELD TESTING PROCEDURES

Field testing was conducted at a contact sulfuric acid plant. The facility contained a series of three-stage sulfur burning contact plants of 2000 ton/day capacity. The stacks were 8.5 ft ID by 200 ft high and made of steel. The sampling site was 160 ft above ground level and 80 ft above the inlet breeching. Effluent control was achieved by using double pass absorption at each stage and a Brinks mist eliminator at the outlet.

Samples were isokinetically collected by a team from Midwest Research Institute using the paired-probe method (7). This consisted of running two sampling trains simultaneously with their probes in close proximity (30 mm) so that they essentially sampled the same environment. The following train variations were studied: inclusion of a second filter between the probe and the IPA impinger; inclusion of a second IPA impinger-filter combination after the first one; introduction of 1 ml of concentrated NH_3 solution into the IPA impinger before sampling; introduction of 0.2 g of DMA into the IPA impinger; and introduction of 50 mg of Fe_2O_3 into the IPA impinger. Sulfate analyses, in this series, were performed at Midwest Research Institute using the methyl thymol blue procedure (8).

SECTION 4

RESULTS AND DISCUSSION

ACID MIST AND SO_3 COLLECTION EFFICIENCY

A study of the Method 8 train efficiency for acid mist and SO_3 collection was conducted in a system consisting of two impingerfilter combinations connected in series, followed by a third impinger (Figure 3). This train sampled from a stream containing acid mist or SO_3 and the sulfate collected in each of these five components was measured. A collection efficiency was calculated representing the percentage of the total sulfate found in the first impinger and filter, since these are the components of the standard Method 8 train designed to collect the acid mist and SO_3. Several of the parameters varied were: the sulfate concentration and temperature of the gas streams under analysis, the type of glass fiber filter used, and the flow rate through the sampling train. These results are tabulated in Tables 1 and 2. The greater part of this study was done using SO_3 rather than acid mist. It was felt that SO_3 presented a greater challenge to the method, since any traces remaining in the gas phase or forming very fine particulate would pass through the filter. (Significant concentrations of SO_3 may be present in H_2SO_4 plant stack gases as a result of poor absorber operation [9].)

The data in Tables 1 and 2 shows that the first impinger-filter combination was highly efficient in collecting both acid mist and SO_3. Furthermore, the bulk of the sulfate was collected on the filter; less than 25 percent was usually detected in the first impinger. Table 1 lists the type of glass fiber filter paper employed in each run. The pH values were measured; MSA 1106BH and Gelman AE had values in the 6.2 to 6.7 range, while Reeve-Angel 934AH had a pH of 9.1. Except for one incidence yielding a low collection efficiency value when a Reeve-Angel filter was used (run 9) effects resulting from the

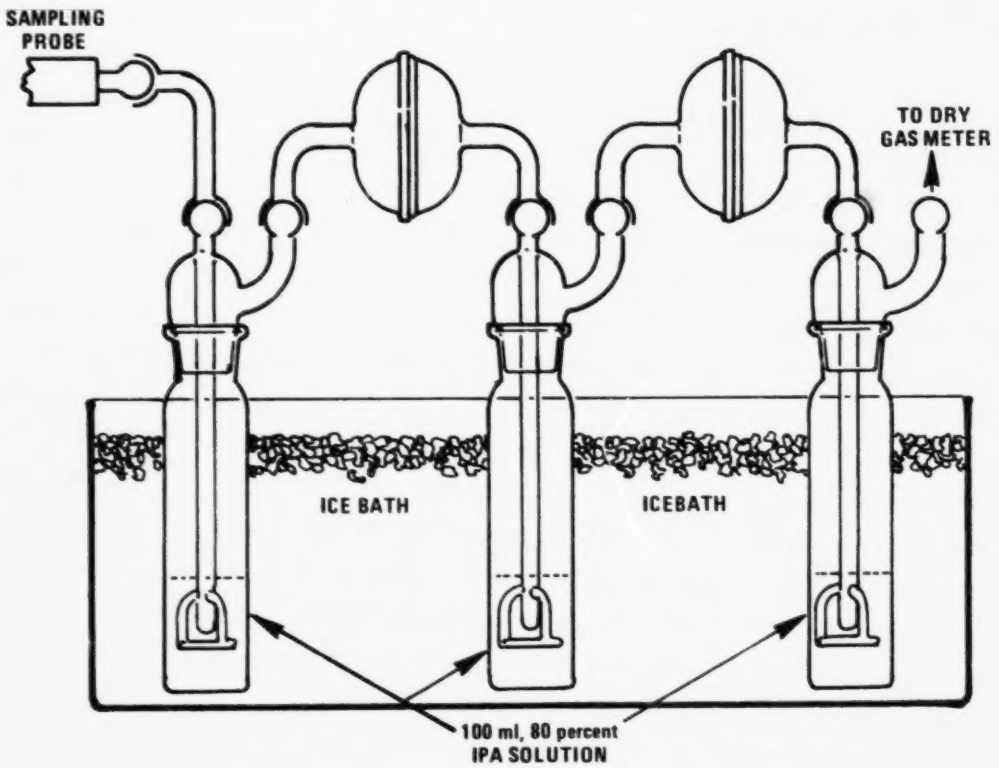

Figure 3. Train used in acid mist collection efficiency study.

TABLE 1. SO_3 SAMPLING DATA AND COLLECTION EFFICIENCY

Run	Sampling rate l/min	Gas temp.	Filter paper	SO_3 Collected, H_2SO_4 mg/m^3						
				1st IPA impinger	1st filter	2nd IPA impinger	2nd filter	3rd IPA impinger	Total collected	% Recovery in 1st impinger & filter
1	21	20	MSA[a]	39.8	143.6	0.7	0.3	0.0	184.4	99
2	21	20	MSA	36.6	59.4	0.1	0.4	0.0	96.5	100
3	16	20	MSA	3.3	19.1	0.1	0.2	0.0	22.7	99
4	31	20	MSA	0.7	11.1	0.5	0.2	0.0	12.5	95
5	21	75	MSA	1.2	3.6	0.1	0.1	0.0	4.9	98
6	21	75	Gel[b]	46.8	213.2	0.7	0.2	9.9	270.8	96
7	21	75	Gel	3.9	14.5	0.4	0.0	0.0	18.8	98
8	30	75	Gel	38.7	248.9	0.2	0.2	0.0	288.0	100
9	35	75	R-A[c]	0.6	2.5	0.2	0.7	0.1	4.0	76
10	16	75	R-A	30.5	385.9	0.1	0.2	0.0	416.7	100
11	20	75	R-A	1.3	17.2	0.1	0.1	0.0	18.7	99
12	20	95	MSA	11.0	21.8	0.4	0.3	0.1	33.6	98
13	20	77	MSA	10.2[d]	16.7	3.1	10.9	0.0	40.9	66

[a]Mine Safety Appliance 1106BH

[b]Type Gelman AE

[c]Reeve Angel 934 AH

[d]Impinger filled with IPA solution to a level below the impaction plate

TABLE 2. ACID MIST SAMPLING DATA AND COLLECTION EFFICIENCY

Run[a]	Gas temp.[b]	Acid mist collected, H_2SO_4 mg/m^3						% Recovery in 1st impinger & filter
		1st IPA impinger	1st filter	2nd IPA impinger	2nd filter	3rd IPA impinger	Total collected	
1	20	12.5	3.9	1.0	0.3	0.2	17.8	92
2	20	6.2	115.9	0.2	0.1	0.0	122.4	100
3	70	15.1	114.9	0.5	0.0	0.0	130.5	100
4	91	11.8	53.3	0.2	0.3	0.0	65.6	99
5	70	13.8[c]	43.6	0.0	0.1	0.0	57.5	100

[a]MSA 1106 BH filters and sampling rates of 21 lpm were used throughout this series.

[b]°C

[c]Impinger filled with IPA solution to a level below the impaction plate

variation of filter type were undetected. The effect of flow rate through the sampling train was also considered. Flow rate was varied from 16 to 34 l/min, the range over which the Greenburg-Smith impinger has been shown to be efficient (10). Low flow rates (runs 3 and 10) did not produce poor collection. In one instance (run 9), poor collection resulted at a higher rate, but this was unconfirmed; thus, the collection efficiency remained relatively constant over the range of sampling flow rates studied. Sulfate concentrations generated varied from 4 to 400 H_2SO_4 mg/m^3 without any apparent effect on the collection efficiency.

When sampling was carried out from heated gas streams, it was noted that the gas rapidly cooled upon entering the Greenburg-Smith impinger resulting in the evaporation of the IPA solution. After two hours of sampling, the alcohol was often depleted to a level below that of the impinger impaction plate. Nonetheless, excellent collection of both acid mist and SO_3 resulted. During a further evaluation, sampling was carried out with the IPA level below the impaction plate throughout the entire run. Acid mist was still collected efficiently (run 5 Table 2) but very poor collection of SO_3 resulted (run 13, Table 1). The quantity of moisture in the first impinger was apparently insufficient to cause the complete hydration of SO_3, since acid mist formation was observed in the second impinger. The results indicated the necessity of maintaining the IPA solution above the level of the impinger impaction plate for efficient SO_3 collection.

EFFICIENCY OF SO_2 COLLECTION

The first part of the Method 8 collecting train, consisting of a Greenburg-Smith impinger containing isopropanol-water solution plus a glass fiber filter, is designed to collect acid mist and to separate it from SO_2. For the most part, SO_2 remains in the gas phase and is subsequently collected in 3 percent H_2O_2 solution in a latter portion of the train. A small amount of SO_2 dissolves in the IPA solution, but is removed by purging. However, since the quantity of SO_2 under analysis is large when compared with acid mist, measurements were conducted to determine if SO_2 was retained in the train components used for acid mist collection. If such were the case, spurious acid mist

values would result. These studies were done using gas streams containing SO_2 and where acid mist was absent.

The results of these measurements are summarized in Table 3, which yielded the following conclusions. Collection of SO_2 in the second and third impingers was carried out with recoveries that varied between 96 and 102 percent. Glass fiber filter extracts yielded measurable quantities of sulfate, but these values were unrelated to the concentration of SO_2 in the gas stream and were negligible when compared with typical acid mist source values. Similar results were obtained when the filter support disc was also extracted and measured for sulfate (runs 27 and 28). However, sulfate was found in the IPA solution of the first impinger in substantial amounts when compared with the quantity of acid mist encountered in a typical compliance analysis. Acid mist compliance values between 14 and 32 mg/m^3 (see Appendix B) and values of approximately 4 mg/m^3 were found in runs 26 through 32. (Roughly the same volume of gas, 0.57 m^3 was collected in each of these runs.) Thus, the passage of SO_2 through the sampling train resulted in spurious acid mist values ranging from 12 to 28 percent of the compliance value.

The amounts of H_2SO_4 collected remained relatively constant even though the concentration of SO_2 in the gas stream under analysis was varied by a factor of four. Increasing the flush time from 15 min (runs 26 through 33) to 30 min (runs 34 through 37) did not decrease the quantity of H_2SO_4 collected. Furthermore, no change was observed when additional H_2SO_4 was added to the IPA before sampling (runs 29 and 33) or when acetone was added (runs 36 A and B). However, when a second IPA impinger was placed in series with the first (run 35B), the same amount of H_2SO_4 was collected as in the first impinger. Also, an impinger containing twice as much IPA solution (run 37B) collected twice as much H_2SO_4. These results indicated that the collection of SO_2 and its conversion to H_2SO_4 resulted from the oxidation of the SO_2 by a substance contained in the IPA solution. This was confirmed when IPA which had been redistilled was employed over $SnCl_2$ (run 37A) and the amount of H_2SO_4 collected was greatly reduced.

TABLE 3. SO_2 COLLECTION IN METHOD 8 TRAIN

Run	SO_2 Concentration, mg/m^3		H_2SO_4 recovered, mg	
	Prepared	Measured[a]	IPA Solution	Filter
26	531	512	2.54	0.30
27	531	522	3.11	0.02[b]
28	527	526	2.25	0.16[c]
29	1030	1022	2.20	0.18
30	983	997	2.61	0.01
31	1047	1028	2.19	0.06
32A	1084	1038	2.20	0.02
32B	0	0	0.00	0.00
33	813	826	2.16	0.02
34	2013	2057	2.18	0.04
35A	1030	-	8.93[d]	-
35B	1030	-	2.37	-
36A	1030	-	2.20	0.02
36B	1030	-	2.38	0.02
37A	1030	-	0.04[e]	0.04
37B	1030	-	4.30	0.04

[a]Quantity collected in two impingers containing 3 percent H_2O_2.

[b]0.15 mg also detected on filter disc.

[c]0.04 mg also detected on filter disc.

[d]IPA solution not flushed.

[e]IPA solution distilled over $SnCl_2$.

The occurrence of oxidants in the IPA observed here should not be regarded as an isolated example. Diisopropyl ether, a substance which readily forms peroxides (11) is employed in the manufacture of anhydrous IPA. When samples of IPA from a number of commercial sources were tested for peroxides, a serious contamination problem was often encountered. The test employed was the KI - peroxide test (see Table 4).

The IPA solution producing the spurious acid mist values listed in Table 4 gave an absorbance of 0.660 when tested. However, Table 4 also contains another entry at least three times that value. It is therefore highly probable that seriously contaminated IPA has been employed in the past in Method 8 source testing and has resulted in spurious acid mist values. Thus, is recommended that all samples of IPA be tested for peroxides prior to being employed in Method 8 measurements, and that the method be modified to include the KI test, herein described. Peroxides can be removed from IPA by distillation over $SnCl_2$ or by passage through an activated alumina column. The latter procedure is more convenient and was employed for all subsequent measurements made in this study.

TABLE 4. RELATIVE H_2O_2 LEVELS IN IPA FROM VARIOUS SOURCES

Commercial source	Lot	Absorbance[a]
Fisher Spectranalyzed	755378	0.660
Fisher Spectranalyzed	753162	0.080
Arthur H. Thomas	?	0.050
Baker Analyzed	607031	0.517
Mallinckrodt AR	CSV	1.978
Occidental Chemical Co.	?	0.025

[a]Absorbance resulting at end of 1.0 min in a 1 cm path cell containing a 1:1 mixture of IPA and 10 percent KI.

INTERACTION OF ACID MIST AND SO_2

To further investigate the mechanisms that might produce spurious acid mist production, the possibility was investigated that SO_2 was catalytically oxidized by the H_2SO_4 collected on the glass fiber filter. This study employed the train shown in Figure 3; the sole modificatio involved the last impinger which contained 3 percent H_2O_2 solution to collect the SO_2. The gas stream analyzed consisted of 5.5 percent O_2 in N_2, and had SO_2 concentrations as listed in Table 5 and a temperature of 75°C. Solution containing H_2SO_4 was measured onto glass fiber filters and air dried. The quantity added corresponded to the amount of H_2SO_4 that would be collected from the gas stream at the end of 2 hrs, if the acid mist concentration were in the 11 to 24 mg/m^3 range. The molar quantity of SO_2 that passed through the sampling train was from 100 to 250 times greater than that of the H_2SO_4 placed on the filter paper.

The following results are evident from Table 5. The single H_2O_2 containing Greenburg-Smith impinger collected SO_2 in good yield. Only traces of H_2SO_4 were found in the IPA containing impingers. Sulfuric acid recovered from the glass fiber filters equalled the amounts added within experimental error in three out of four instances. On the first filter of run 2, an excess amount was detected corresponing d to an acid mist value of 0.4 mg/m^3. Thus, if oxidation of SO_2 took place, it did so at a level at or below the detection limits of these measurements. Furthermore, the SO_2 concentrations employed were approximately four times greater than those encountered at a typical source. Therefore, we must conclude that H_2SO_4 does not promote the oxidation of SO_2 to the extent of causing a significant acid mist interference.

A further attempt to find evidence for the interference of SO_2 in acid mist measurements was carried out as follows.

Suspended acid mist particulate was produced in heated gas streams consisting of 5.5 percent O_2 in N_2. A gas manifold was utilized allowing SO_2 the addition of and enabling samples to be withdrawn both before and after the point of SO_2 introduction. The gas manifold was described earlier. Parallel

TABLE 5. TEST FOR SO_2 OXIDATION ON GLASS FIBER FILTERS CONTAINING ADDED H_2SO_4

Run	H_2SO_4 mmoles						Volume m^3	SO_2 mg/m^3		% Recovery
	1st IPA impinger	1st Filter		2nd IPA impinger	2nd Filter					
		Added	Found		Added	Found		Added	Found	
1	0.008	0.300	0.297	0.010	0.600	0.593	2.456	1801	1811	100.6
2	0.001	0.248	0.261	0.001	0.248	0.244	2.366	1800	1749	97.2

samples were withdrawn by two Method 8 trains operating simultaneously. Acid mist concentrations were measured and the results are presented in Table 6.

TABLE 6. EFFECTS OF SO_2 ON ACID MIST COLLECTION

Run	H_2SO_4 mg/m^3		%	SO_2 Added
	SO_2 Absent	SO_2 Present	Deviation	mg/m^3
1	4.12	4.43	8	1030
2	10.95	13.15	20	840
3	30.8	38.2	24	1230
4	72.1	49.6	-31	1190
5	98.9	120.1	21	0
6	39.6	43.0	9	0
7	18.0	18.3	2	0
8	33.1	32.9	-1	0
9	18.8	18.6	-1	3200
10	17.8	19.9	12	1400

It seems impossible to draw definite conclusions from this data. Acid mist values measured before and after the SO_2 addition neither agreed nor showed a consistent trend. The observed deviations, ranging from -31 to +24 percent, took place when SO_2 was absent and did not correlate with SO_2 concentrations when the latter substance was added. Clearly, these differences represent fluctuations introduced by experimental factors, rather than chemical interactions between acid mist and SO_2. Thus, the data only allows us to place an upper limit on such interactions. Consequently, when it was noted that these measurements employed SO_2 concentrations as much as eight times greater than typical source values, this series of experiments added weight to the other results reported in this study. Based on this data and on our failure to find evidence for the oxidation of SO_2 to H_2SO_4 in IPA impingers or on glass fiber filters, it must be concluded that SO_2 does not interfere in acid mist measurements.

DISCUSSION OF METHODOLOGY

During the course of the preceding study, it became necessary to prepare filters containing a known amount of H_2SO_4. The initial filters made were dried in an oven. Discoloration resulted and the added H_2SO_4 could only be partially recovered. The variety of filter paper employed (MSA 1106BH) contains approximately 0.5 percent organic binder. It became evident that oxidation of the filter paper binder had taken place with a resultant loss of H_2SO_4. When H_2SO_4 was added to filters that were subsequently dried at ambient temperatures, no discoloration resulted and good recoveries of H_2SO_4 were made. These measurements were repeated several times and the results are listed in Table 7. The filter employed in EPA Method 8 remains at or below ambient temperatures where loss of H_2SO_4 is absent. However, we have received suggestions for the design of other techniques which the heating of filters for use with sources possibly containing H_2SO_4. The results in Table 7 indicate that such alternative methods would have to employ glass fiber filters practically free of organic binder in order to avoid collected acid mist losses or a reduction in the filter "tare."

TABLE 7. H_2SO_4 INTERACTION WITH GLASS FIBER FILTERS

Sample	H_2SO_4, mmoles		%
	Added	Found	Recovery
Pipette calibration	0.300	0.301	100.3
Pipette calibration	0.300	0.299	99.6
Oven dried. temp. & time	0.300	0.189	63.1
not recorded. Charring.	0.300	0.208	69.4
Pipette calibration	0.250	0.248	99.2
Pipette calibration	0.250	0.251	100.2
Dried at ambient temperature	0.250	0.245	98.1
no darkening of filter	0.250	0.248	99.1
	0.250	0.240	96.2
Filter dried at 160°C, 2 h	0.250	0.136	54.5
Charring of paper observed	0.250	0.133	53.3
	0.250	0.154	61.7

The barium-thorin analytical method is based on the insolubility of barium sulfate ($BaSO_4$) and the formation of a colored complex between barium ions and thorin indicator. During the course of this and related studies, both barium chloride ($BaCl_2$) and barium perchlorate ($Ba[ClO_4]_2$) have been employed as titrants. Experience has shown that the use of $BaCl_2$ results in end points that are not as sharply lineated. This may be caused by the formation of a complex between barium and chloride ions which competes with the barium-thorin complex. The use of a $Ba(ClO_4)_2$ as the titrant is therefore preferable.

Difficulty in detecting the yellow-pink color change which occurs at the barium-thorin end point prompted the investigation of other indicators. Sulfanazo III and thorin-xylene cyanol FF mixtures were studied. Both of these indicators give sharp, easily observable end points, when low sulfate concentrations are measured. However, sulfanazo III and xylene cyanol FF dyes are strongly absorbed on $BaSO_4$ precipitate, so that continuous color changes take place during titration. This effect is especially pronounced when high sulfate concentrations are being determined. Since high sulfate concentrations often occur during source sampling, both of these indicators are unsuitable for such measurements.

FIELD TESTING

Field testing was carried out to study several variations of the Method 8 sampling procedure under the rigorous conditions of actual use. Each variation was tested simultaneously with a standard Method 8 train, using the paired-probe method. Sulfate analysis was carried out by the methyl-thymol blue method previously mentioned (8). This procedure was employed because only the sample collection part of Method 8 was under consideration in the field tests. In addition, NH_3, DMA, and Fe_2O_3, which were employed in this study, do not interfere in the methylthymol blue procedure (12,13), but do interfere in barium-thorin analyses under certain conditions (3). The results are listed in Table 8; values obtained using the Method 8 train are designated as A and train variations are designated as B.

Effect of Purge Time Variation

In the first test, Train B was purged for only 4 min at the end of the sampling run, while Train A was purged for the full 15 min specified in the Method 8 procedure (sample 1 and 2). There is no evidence of SO_2 retention in the IPA impingers flushed for only 4 min, nor do the SO_2 values from Train A appear to be increased as a result of ambient SO_2 collection.

Acid Mist Collection Efficiency

To test the efficiency of acid mist collection, a second IPA impinger and a filter were placed immediately after the first combination. Moderately high vacuums were encountered on Train B due to the extra filter. Results of the sulfate analysis of the probe, the first IPA impinger, and the first filter, are listed under the acid mist column of Table 8 (3B and 4B). Results of the analysis of the second IPA impinger and the second filter are designated 3B' and 4B'. There is some indication that sulfate was detected in the second IPA impinger-filter combination in sampling run no. 3. However, very low acid mist values were encountered in this study. The analytical blank corresponded to 3.6 mg of H_2SO_4/m^3 so that the value listed as 3B' represented barely more than a trace amount. The quantity of sulfate detected in Sample 4B' was too small to measure. Thus, samples 3 and 4 do not provide conclusive evidence; however, they do indicate that at least the bulk of the acid mist is collected in the first IPA impinger-filter combination.

The configuration adopted in sampling runs no. 5 and 6 consisted of a filter, an IPA impinger, and another filter, followed by the peroxide impingers. The first filter and the probe were analyzed separately for sulfate and results are reported in the acid mist column of Table 8 for samples no. 5B and 6B. The IPA impinger and the second filter were analyzed together and the results are reported as samples 5B' and 6B'. This data shows that all of the acid mist was collected in the probe and on the first filter. Sample no. 6 is particularly significant because sulfate values were encountered which were substantially above trace levels.

TABLE 8. METHOD 8 TRAIN COMPARED WITH OTHER CONFIGURATIONS USING PAIRED PROBE SAMPLING

Sample No.	Special conditions employed in Train B	Gas vol. sampled, standard m^3	Acid mist, H_2SO_4 mg/m^3	SO_2,[3] mg/m^3
1A[a]		1.087	6.0	381
1B	4 min purge	1.073	5.0	372
2A		1.156	trace	372
2B	4 min purge	1.172	trace	380
3A		1.130	2.1[b]	742
3B	Second IPA impinger	1.134	1.7[b]	685
3B'	and filter	-	0.8[c]	-
4A		1.163	0.7[b]	356
4B	Second IPA impinger	1.146	1.1[b]	335
4B'	and filter	-	trace[c]	-
5A		1.122	1.1[d]	355
5B	Second filter	1.110	1.3[d]	359
5B'	before IPA impinger	-	trace[e]	-
6A		1.255	6.5[d]	440
6B	Second filter	1.251	4.4[d]	433
6B'	before IPA impinger	-	trace[e]	-
7A		1.276	5.1	393
7B	NH_3 in IPA impinger	1.235	57.6	273
8A		1.323	5.0	386
8B	DMA in IPA impinger	1.304	98.0	200
9A		1.275	6.1	373
9B	Fe_2O_3 in IPA impinger	1.266	0.5	359

[a]Sample designation A denotes use of standard Method 8 train.

[b]Value obtained from first IPA impinger-filter combination.

[c]Value obtained from second IPA impinger-filter combination.

[d]Value obtained from first filter.

[e]Value obtained from second filter and IPA impinger.

A method that has been employed for sulfuric acid plant analysis - the Monsanto Method (12) - determines sulfate from the extract of the sampling probe and a glass fiber filter. It is similar to EPA Method 8, except that the latter method also employs an IPA impinger before the filter. From these results, combined with the laboratory evaluations we can conclude that a filter, not preceded by an IPA impinger, will collect sulfuric acid mist efficiently; however, accurate results can only be expected when SO_3 is absent from the gas stream. For the latter compound to be collected on a glass fiber filter, a hydration mechanism is required, such as the one provided in the IPA solution specified in Method 8.

Efficiency of SO_2 Collection

The results in Table 8 show that the paired-probe trains agreed within $\pm$ 1 percent in samples 1, 2, 5, and 6. Agreement in samples 3 and 4 was $\pm$ 4 and 3 percent, respectively. These sampling runs employed a second impinger-filter combination and a higher train vacuum. Consequently, this may have caused a slight, intermittant leakage diluting the sample and resulting in lower values. On the other hand, $\pm$ 4 percent is not considered large in source sampling; thus, it is a fair judgement that good agreement was obtained between paired-probe train SO_2 values in the entire series of samples 1 through 6. This is evidence that the experimental train variations employed in this series did not disrupt train functioning.

Effect of Interferents

Ammonia (NH_3) has been employed in SO_2 scrubbers and their tail gas streams may contain as much as 0.03 percent NH_3 vapor (15). At that concentration, gas collected at a 28 l/min sampling rate for 2 h would contain a total of 40 mmoles of NH_3. To approximate these conditions, 15 mmoles of NH_3 were added to the IPA solution in the first impinger, prior to sampling. When sampling was conducted the formation of a white solid was observed [NH_4HSO_3] which eventually plugged the filter, requiring an interruption of the run plus a filter change. At the conclusion of sampling, the odor of NH_3 was no longer

detected in the IPA impinger. Methylthymol blue analysis of the combined extract of the IPA impinger and the filter from the train with added NH_3, yielded a sulfate value more than 10 times that of the control train (see Table 8). The methylthymol blue method determines sulfite as well as sulfate (8). The measurement value obtained from the NH_3 containing train corresponded to 1.6 milliequivalents of SO_2. Since 15 milliequivalents of NH_3 was added, this would indicate that much of the NH_3 had been purged out of the IPA impinger. However, the degree of SO_2 retention was sufficiently large that serious interferences may be expected if Method 8 is used to measure sulfate emissions in effluent streams containing NH_3 vapor.

Dimethlanaline is another material used in scrubbers to control SO_2 emissions. In order to simulate conditions (16) that may occur after sampling effluents from DMA scrubbers, 3.3 milliequivalents of DMA were added to the IPA impinger and the results were compared with a standard Method 8 train (see Table 8). Analysis indicated that 3.8 milliequivalents of excess SO_2 were detected in the IPA impinger extract and the filter of the train with added DMA. However, the total amount of SO_2 measured in the latter train was considerably less than that measured in the standard Method 8 train; therefore, the presence of DMA may have caused some analytical difficulty, in addition to producing a large positive interference in the sulfate value. Sulfuric dioxide values obtained when NH_3 and DMA were present showed poor agreement with the corresponding paired-probe train values. This remained true in samples 7 and 8 even when the "acid mist" values of Train B were added to the SO_2 values and compared with the quantity of SO_2 determined in Train A. It can only be concluded that the presence of NH_3 and DMA caused a general disruption of both the sampling and the analytical procedures and produced meaningless results.

The use of Method 8 at steel pickling plants prompted us to study the effects of ferric oxide (Fe_2O_3) on Method 8 train operations. Approximately 1.2 milliequivalents of iron were added to the IPA impinger; Table 8 shows that a negative interference in the sulfate measurement resulted. Agreement between the SO_2 values of Trains A and B was fair, so it appears that the presence of Fe_2O_3 affected only the acid mist determination.

EVALUATION OF SOLID AMMONIUM SULFATE AS AN AUDIT MATERIAL

It would prove invaluable to have a solid substance to aid in the preparation of audit samples for barium-thorin analysis. Audit samples prepared from a solid sulfate would be independent of the H_2SO_4 solution used for calibration and would be useful, not only for evaluating the operator, but also for detecting calibration errors. For these reasons, we carried out the following comparison study and selected solid ammonium sulfate $(NH_4)_2SO_4$ as the candidate material.

Barium perchlorate ($Ba[ClO_4]_2$) solution was prepared as described in Method 8 and standardized against standard acid. The results are listed in the first column of Table 9. A stock solution of $(NH_4)_2SO_4$ was prepared from reagent-grade salt that had been dried for 2 h at 110°C. The $(NH_4)_2SO_4$ solution had the same normality as the standard acid, 0.01013N. The results of its barium-thorin analysis appear in the second column of Table 9. An additional test was conducted employing $(NH_4)_2SO_4$ solutions produced by adding measured amounts of NH_3 to aliquots of standard H_2SO_4 solution. These were analyzed by the barium-thorin method (see Table 9).

TABLE 9. COMPARISON OF BARIUM THORIN ANALYSIS OF H_2SO_4 AND $(NH_4)_2SO_4$ SOLUTIONS

	$Ba(ClO_4)_2$ Solution, ml		
	Standard H_2SO_4	$(NH_4)_2SO_4$[a] Solution	NH_3 Standard H_2SO_4
	26.35	25.60	26.41
	26.79	25.66	27.43
	26.82	25.62	26.90
	26.42	-	26.82
MEAN	26.613	25.627	26.890

[a]Prepared from solid $(NH_4)_2SO_4$.

The following conclusions may be drawn from the data in Table 9. Measurement of the solution prepared from solid $(NH_4)_2SO_4$ yielded values that were slightly low - 96.3 percent of the gravimetric value. The discrepancy is real, because a statistical treatment of the pooled data in the first and second columns shows the difference between the two means to be significant at the 95 percent confidence level. A similar treatment of the data in the first and third columns shows that those differences are insignificant.

Thus, barium-thorin analysis of a solution prepared from solid $(NH_4)_2SO_4$ yielded results approximately (96.3%) equal to the prepared value. The discrepancy from 100 percent was apparently real and may have been caused by impurities in the salt or by a calibration bias. The presence of a stochiometric amount of NH_3 did not produce an interference. Therefore, solid $(NH_4)_2SO_4$ shows promise for future use as an audit material in barium-thorin analysis, although additional work will be necessary before this material can be established as a calibration standard.

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METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide, and in the absence of other particulate matter) and sulfur dioxide emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 milligrams/cubic meter (0.03×10^{-7} pounds/cubic foot) for sulfur trioxide and 1.2 mg/m³ (0.74×10^{-7} lb/ft³) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m³ (35.3 ft³) gas sample is about 13,500 mg/m³ (7.7×10^{-4} lb/ft³). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents are present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, U S EPA are required. 87

Filterable particulate matter may be determined along with SO_3 and SO_2 (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see Section 2.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only. H_2SO_4 acid mist is not determined separately. 87

2. *Apparatus*

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 8-1; it is similar to the Method 5 train except that the filter position is different and the filter holder does not have to be heated. Commercial models of this train are available. For those who desire to build their own, however, complete construction details are described in APTD-0581 Changes from the APTD-0581 document and allowable modifications to Figure 8-1 are discussed in the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Further details and guidelines on operation and maintenance are given in Method 5 and should be read and followed whenever they are applicable.

2.1.1 Probe Nozzle. Same as Method 5, Section 2.1.1.

2.1.2 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

2.1.3 Pitot Tube. Same as Method 5, Section 2.1.3.

2.1.4 Differential Pressure Gauge. Same as Method 5, Section 2.1.4.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials, e.g., Teflon or Viton, may be used subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Note: Do not heat the filter holder.

2.1.6 Impingers—Four, as shown in Figure 8-1. The first and third shall be of the Greenburg-Smith design with standard tips. The second and fourth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in.) ID glass tube, having an unconstricted tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.1.7 Metering System. Same as Method 5, Section 2.1.8.

2.1.8 Barometer. Same as Method 5, Section 2.1.9.

2.1.9 Gas Density Determination Equipment. Same as Method 5, Section 2.1.10.

2.1.10 Temperature Gauge. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1° C (2° F).

2.2 Sample Recovery.

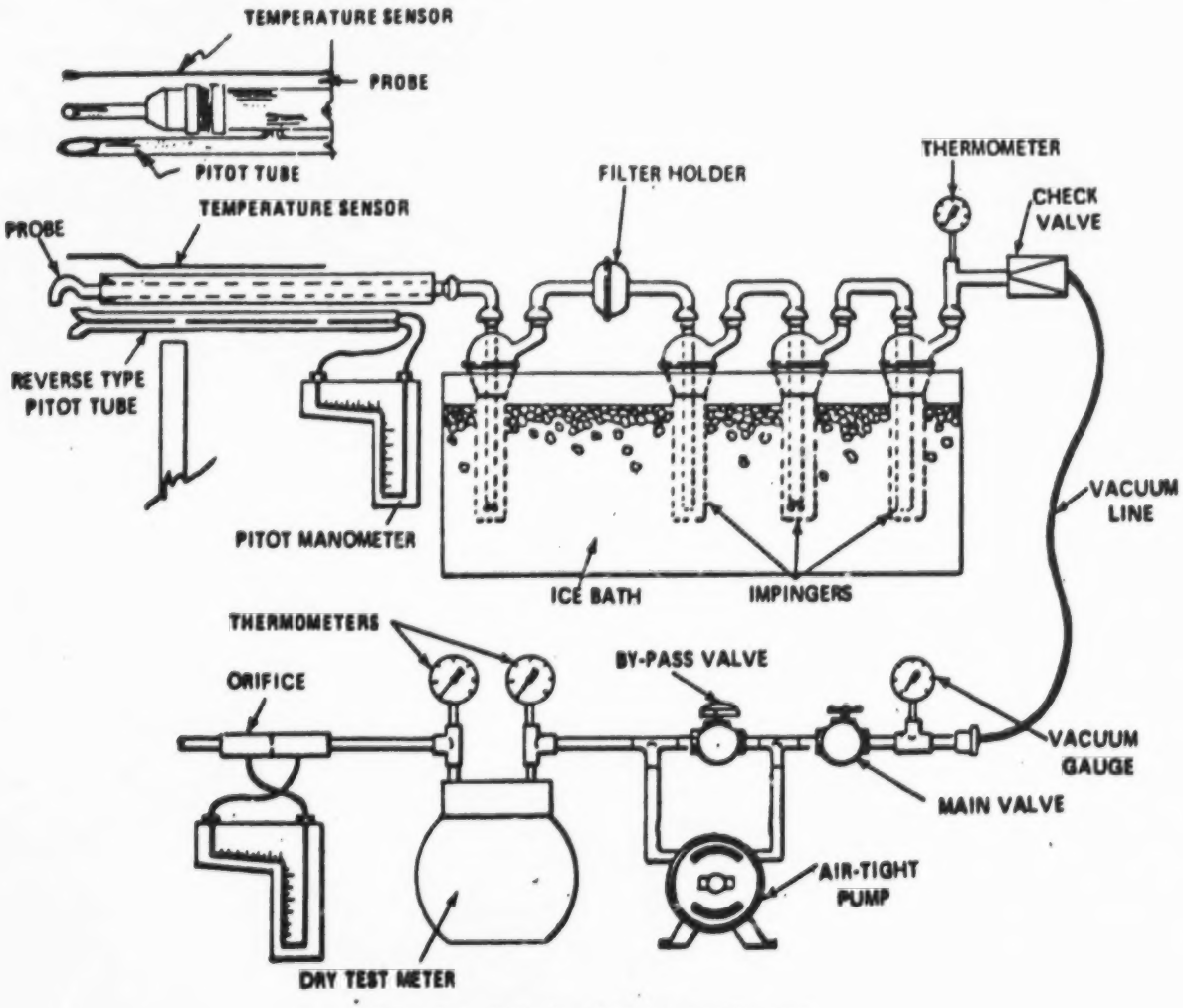

Figure 8-1. Sulfuric acid mist sampling train.

3.2.1 Wash Bottles. Polyethylene or glass, 500 ml. (Two).

3.2.2 Graduated Cylinders. 250 ml, 1 liter. (Volumetric flasks may also be used.)

3.2.3 Storage Bottles. Leak-free polyethylene bottles, 1000 ml size (two for each sampling run).

3.2.4 Trip Balance. 500-gram capacity, to measure to ±0.5 g (necessary only if a moisture content analysis is to be done).

3.3 Analysis.

3.3.1 Pipettes. Volumetric 25 ml, 100 ml.

3.3.2 Burette. 50 ml.

3.3.3 Erlenmeyer Flask. 250 ml. (one for each sample blank and standard).

3.3.4 Graduated Cylinder. 100 ml.

3.3.5 Trip Balance. 500 g capacity, to measure to ±0.5 g.

3.3.6 Dropping Bottle. To add indicator solution, 125-ml size.

4. *Reagents*

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

4.1 Sampling.

4.1.1 Filters. Same as Method 5, Section 3.1.1.

4.1.2 Silica Gel. Same as Method 5, Section 3.1.2.

4.1.3 Water. Deionized, distilled to conform to ASTM specification: D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

4.1.4 Isopropanol, 80 Percent. Mix 800 ml of isopropanol with 200 ml of deionized, distilled water.

NOTE.—Experience has shown that only A.C.S. grade isopropanol is satisfactory. Tests have shown that isopropanol obtained from commercial sources occasionally has peroxide impurities that will cause erroneously high sulfuric acid mist measurement. Use the following test for detecting peroxides in each lot of isopropanol: Shake 10 ml of the isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance on a spectrophotometer at 352 nanometers. If the absorbance exceeds 0.1, the isopropanol shall not be used. Peroxides may be removed from isopropanol by redistilling, or by passage through a column of activated alumina. However, reagent-grade isopropanol with suitably low peroxide levels is readily available from commercial sources; therefore, rejection of contaminated lots may be more efficient than following the peroxide removal procedure.

4.1.5 Hydrogen Peroxide, 3 Percent. Dilute 100 ml of 30 percent hydrogen peroxide to 1 liter with deionized, distilled water. Prepare fresh daily.

4.1.6 Crushed Ice.

4.2 Sample Recovery.

4.2.1 Water. Same as 3.1.3.

4.2.2 Isopropanol, 80 Percent. Same as 3.1.4.

4.3 Analysis.

4.3.1 Water. Same as 3.1.3.

4.3.2 Isopropanol, 100 Percent.

4.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

4.3.4 Barium Perchlorate (0.0100 Normal). Dissolve 1.95 g of barium perchlorate trihydrate ($Ba(ClO_4)_2 \cdot 3H_2O$) in 200 ml deionized, distilled water, and dilute to 1 liter with isopropanol. 1.22 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times.

4.3.5 Sulfuric Acid Standard (0.0100 N). Purchase or standardize to ±0.0002 N against 0.0100 N NaOH that has previously been standardized against primary standard potassium acid phthalate.

4. *Procedure*

4.1 Sampling.

4.1.1 Pretest Preparation. Follow the procedure outlined in Method 5, Section 4.1.1; filters should be inspected, but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry, i.e., moisture free, the silica gel need not be weighed.

4.1.2 Preliminary Determinations. Follow the procedure outlined in Method 5, Section 4.1.2.

4.1.3 Preparation of Collection Train. Follow the procedure outlined in Method 5, Section 4.1.3 (except for the second paragraph and other obviously inapplicable parts) and use Figure 8-1 instead of Figure 5-1. Replace the second paragraph with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent hydrogen peroxide in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

PLANT _____

LOCATION _____

OPERATOR _____

DATE _____

RUN NO. _____

SAMPLE BOX NO. _____

METER BOX NO. _____

METER ΔH@ _____

C FACTOR _____

PITOT TUBE COEFFICIENT, Cp _____

SCHEMATIC OF STACK CROSS SECTION

STATIC PRESSURE, mm Hg (in. Hg) _____

AMBIENT TEMPERATURE _____

BAROMETRIC PRESSURE _____

ASSUMED MOISTURE, % _____

PROBE LENGTH, m (ft) _____

NOZZLE IDENTIFICATION NO. _____

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____

PROBE HEATER SETTING _____

LEAK RATE, m^3/min, (cfm) _____

PROBE LINER MATERIAL _____

FILTER NO. _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_s), °C (°F)	VELOCITY HEAD (ΔP_s), mm H_2O (in. H_2O)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER, mm H_2O (in. H_2O)	GAS SAMPLE VOLUME, m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET, °C (°F)	OUTLET, °C (°F)	
TOTAL							Avg	Avg	
AVERAGE							Avg		

Figure 8-2. Field data.

NOTE.—If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g and record these weights. The weight of the silica gel (or silica gel plus container) must also be determined to the nearest 0.5 g and recorded.

4.1.4 Pretest Leak-Check Procedure. Follow the basic procedure outlined in Method 5, Section 4.1.4.1, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as, "* * * plugging the inlet to the filter holder * * *," shall be replaced by, "* * * plugging the inlet to the first impinger * * *." The pretest leak-check is optional. [87]

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m³/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in Section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as in Section 4.1.4.3 of Method 5 (with appropriate modification) and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, the tester shall either correct the sample volume, as outlined in Section 6.3 of Method 5, or shall void the run.

Drain the ice bath and, with the probe disconnected, purge the remaining part of the train, by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE.—Clean ambient air can be provided by passing air through a charcoal filter. At the option of the tester, ambient air (without cleaning) may be used.

4.1.6 Calculation of Percent Isokinetic. Follow the procedure outlined in Method 5, Section 4.1.6.

4.2 Sample Recovery.

4.2.1 Container No. 1. If a moisture content analysis is to be done, weigh the first impinger plus contents to the nearest 0.5 g and record this weight.

Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml with 80 percent isopropanol. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution against evaporation. Mark the level of liquid on the container and identify the sample container. [87]

4.2.2 Container No. 2. If a moisture content analysis is to be done, weigh the second and third impingers (plus contents) to the nearest 0.5 g and record these weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

Transfer the solutions from the second and third impingers to a 1000-ml graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with deionized, distilled water, and add this rinse water to the cylinder. Dilute to a volume of 1000 ml with deionized, distilled water. Transfer the solution to a storage container. Mark the level of liquid on the container. Seal and identify the sample container.

4.3 Analysis.

Note the level of liquid in containers 1 and 2, and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

4.3.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater. [87]

4.3.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

5. *Calibration*

5.1 Calibrate equipment using the procedures specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); Section 5.7 (barometer). Note that the recommended leak-check of the metering system, described in Section 5.6 of Method 5, also applies to this method.

5.2 Standardize the barium perchlorate solution with 25 ml of standard sulfuric acid, to which 100 ml of 100 percent isopropanol has been added.

6. *Calculations*

Note.—Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m² (ft²).

B_{ws} = Water vapor in the gas stream, proportion by volume.

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf). [87]

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf). [87]

I = Percent of isokinetic sampling.

N = Normality of barium perchlorate titrant, g equivalents/liter.

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg). [87]

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg). [87]

T_m = Average absolute dry gas meter temperature (see Figure 8-2), ° K (° R).

T_s = Average absolute stack gas temperature (see Figure 8-2), ° K (° R).

T_{std} = Standard absolute temperature, 293° K (528° R). [87]

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2.

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf). [87]

v_s = Average stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 8, m/sec (ft/sec).

V_{soln} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively. [87]

V_t = Volume of barium perchlorate titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

ΔH = Average pressure drop across orifice meter, mm (in.) H_2O.

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 8-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C and 760 mm Hg or 68° F and 29.92 in. Hg) by using Equation 8-1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right) \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Equation 8-1

where:

K_1 = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

NOTE.—If the leak rate observed during any mandatory leak-checks exceeds the specified acceptable rate, the tester shall either correct the value of V_m in Equation 8-1 (as described in Section 6.3 of Method 5), or shall invalidate the test run.

6.4 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor using Equation 5-2 of Method 5; the weight of water collected in the impingers and silica gel can be directly converted to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas, using Equation 5-3 of Method 5. The "Note" in Section 6.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric acid mist (including SO_3) concentration.

$$C_{H_2SO_4} = K_2 \frac{N(V_t - V_{tb})\left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 8-2

where:

K_2 = 0.04904 g/milliequivalent for metric units.
= 1.081×10^{-4} lb/meq for English units.

6.6 Sulfur dioxide concentration.

$$C_{SO_2} = K_2 \frac{N(V_t - V_{tb})\left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}}$$

Equation 8-3

where:

K_2 = 0.03203 g/meq for metric units.
= 7.061×10^{-4} lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

$$I = \frac{100\, T_s [K_4 V_{lc} + (V_m Y / T_m) P_{bar} + \Delta H/13.6)]}{60\, \theta\, V_s P_s A_n}$$

Equation 8-4 [87]

where:

K_4 = 0.003464 mm Hg-m³/ml-°K for metric units.
= 0.002676 in. Hg-ft³/ml-°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std}\, 100}{T_{std} v_s \theta A_n P_s\, 60 (1 - B_{ws})}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})}$$

Equation 8-5

where:

K_5 = 4.320 for metric units.
= 0.09450 for English units.

6.8 Acceptable Results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may opt to accept the results. Use Citation 4 in the Bibliography of Method 5 to make judgments. Otherwise, reject the results and repeat the test.

7. *Bibliography*

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APPENDIX B

ACID MIST PERFORMANCE STANDARD RELATIONSHIPS

Federal regulations (1) state the acid mist performance standard in terms of a maximum quantity which may be discharged into the atmosphere per ton of acid produced; 0.075 Kg of mist/metric ton of H_2SO_4. Method 8, however, determines acid mist as a weight of H_2SO_4 per unit volume of gas sampled and in order to evaluate results obtained in the present study, it is necessary to relate these quantities. The volume of gas exiting a contact acid plant per ton of H_2SO_4 produced varies with the plant and the operating conditions employed. However, in a survey of 40 plants (6), the minimum volume to weight ratio occurred in a plant that produced 150 short tons/day and had an exit gas discharge of 7,940 SCFM. This corresponds to:

$$7{,}940\ ft^3/min\ (1440\ min/day)(0.02832\ m^3/ft^3)(1\ day/150\ short\ tons)(1\ short\ ton/0.908\ m\ ton) = 2370\ m^3\ of\ exit\ gas/metric\ ton\ of\ H_2SO_4\ produced \qquad \text{(Equation A-1)}$$

Relating this to the standard:

$$75{,}000\ mg\ of\ mist/metric\ ton\ of\ acid\ (1\ metric\ ton/2370\ m^3) = 32\ mg\ of\ acid\ mist/m^3 \qquad \text{(Equation A-2)}$$

In the plant under consideration, no dilution air was in use. However, at other plants employing dilution air, this figure can be reduced to as low as 14 mg/m^3.